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Abstract

Textiles are very hazardous materials when related to fires, because of the high surface to mass ratio and the open structure, which simplify the contact with heat and oxygen. Fabrics have a great impact on the development of fatal fires because of their easy ignition and high burning rate. For the flame retardancy of fabrics several strategies have been developed throughout the years, and nowadays additives and reagents are widely used for the different kinds of textiles. The most common commercial durable finishes for cotton fabrics contain phosphorous and nitrogen compounds. These products have been predominant in the field of flame retardants for cotton for 50 years, but recently the request for a reduction of environmental impact and of formaldehyde release during manufacturing and utilisation have pushed researchers towards new kinds of finishing.

This Ph.D. work aimed at investigating the effectiveness and the possibilities of the use of biomacromolecules as fire retardants for cellulosic textiles (i.e. cotton). To this aim, three biomacromolecules were taken in consideration: whey proteins, caseins and nucleic acids.

Whey proteins and caseins, derived from milk, were applied on cotton fabrics and their thermal and thermo-oxidative stability and fire behaviour were assessed through thermogravimetric analysis, cone calorimetry and horizontal flame spread tests. These biomacromolecules were effective in improving the fire retardancy of the treated fabrics, slowing down the combustion rate in flame spread tests and favouring the formation of a coherent carbonaceous residue (char).

Then, the fire retardant behaviour of DNA was thoroughly investigated. First, commercially-available DNA from herring sperm and testes, having different molecular weights, were applied on cotton fabrics: the experimental parameters (i.e., molecular weight of the biomacromolecules, pH of the aqueous solution, number of impregnations needed for achieving the final dry add-on on the treated fabrics) were optimized in order to achieve the highest flame retardant effectiveness. The distribution of the nucleic acids on the underlying fabric was studied through SEM analyses. Thermogravimetric analyses, cone calorimetry and horizontal flame spread tests were carried out for assessing the thermal and thermo-oxidative stability and the fire behaviour of the treated fabrics. In detail, the low-molecular-weight DNA solution prepared either at pH 4 or 8 and applied on cotton with multiple impregnation steps was the most effective flame retardant treatment.

Pursuing the research, the problem related to the high cost of commercially available DNA was considered: to overcome this drawback, a novel extraction method, starting from exhausted biomasses or agro-food crops, was developed. This method focused on the extraction of high quantities of nucleic acids, exploiting a low environmental impact approach. Overall, the recovered nucleic acids showed a fire behaviour similar to that of commercially-available counterparts.

Finally, the washing fastness of the cotton fabrics treated with the biomacromolecules was considered: in fact, all the selected biomacromolecules are waterborne systems, which easily come off the fabrics when subjected to washing cycles, even in hot water only. This issue was taken on by treating cotton fabrics with

nucleic acids and chitosan in mixture or as separate layers and also exploiting the layer by layer technique. The washing fastness of the treated fabrics was significantly improved by subjecting them to UV-curing, thus achieving the grafting of chitosan on cotton and, at the same time, entrapping the nucleic acid in the grafted chitosan coating. Notwithstanding the achieved fire retardancy, the fabrics treated with chitosan and nucleic acids also showed an antibacterial activity, due to the presence of chitosan. Furthermore, 30 bilayers of nucleic acids and chitosan provided the fabrics with self-extinction, either before and after a water washing cycle at 55°C.

As far as the effectiveness of the treatments is concerned, all the selected biomacromolecules conferred fire retardant features to cotton fabrics. In particular, low-molecular-weight nucleic acids and caseins were the most performing biomacromolecules either in forced combustion or in flame spread tests. Cotton fabrics treated with nucleic acids or caseins were able to achieve self-extinction in horizontal flame spread tests, with a reduction of the burning rate and an increase of the residue left. Similar reductions in the HRR were also observed in cone calorimetry tests.

The suggested approach is quite simple and does not involve the use of particular chemicals or expensive equipment; furthermore, the selected biomacromolecules are soluble/dispersible in water.

In conclusion, the proposed flame retardants for cotton may represent a new sustainable approach to face the challenges related to the increasing awareness of the health and environmental impact of traditional products and processes.